The Raman Spectra of Boron Trifluoride, Trichloride, and Tribromide. The Effect of the Boron Isotopes*

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The Raman frequencies $\nu_1\{1\}$, $2\nu_2\{2\}$, $\nu_3\{2\}$, and $\nu_4\{2\}$ for $BF_3(g)$, $BCl_3(l)$, and $BBr_3(l)$ were found to be 886 and 783, 1394, 1038 and 1105, 440; 471, 924, 958 and 996, 243; 279, 743, 806 and 846, and 151 cm^{-1}, respectively. The assignment of frequencies was determined by polarization experiments on BCl_3 and is confirmed for the three compounds by the results of a normal coordinate treatment. The doubling of ν_1 in BF_3 is ascribed to vibrational resonance between ν_1 and $2\nu_4$. The doubling of ν_3 in all three compounds is shown to be due to the presence of the two isotopes of boron B^{10} and B^{11}. A satisfactory assignment of the infrared frequencies of BCl_3 is made.

INTRODUCTION

THE Raman spectrum of boron trichloride has been reported by Bhagavantam and by Venkateswaran.[1] Cassie[2] has proposed an assignment for the infrared frequencies he observed for boron trichloride, but he assumed frequencies differing rather widely from the Raman frequencies as well as the presence of forbidden lines in the infrared spectrum.

We have reinvestigated the Raman spectrum of boron trichloride and report as well the Raman spectra of boron tribromide and boron trifluoride. In all three compounds a doubling of certain frequencies by the presence of the boron isotopes B^{10} and B^{11} is observed. The infrared spectrum of boron trichloride is satisfactorily explained by an assignment of frequencies which is confirmed by the results of a normal coordinate treatment.

The work on boron trifluoride was started at this laboratory in 1934 by Mr. S. T. Gross.

This and other similar investigations were assisted by a grant-in-aid of research to one of us (D. M. Y.) from the National Research Council. The boron tribromide used was prepared as an N.Y.A. project by Mr. David Pressman.

GENERAL THEORETICAL CONSIDERATIONS

The shape of the boron trichloride molecule is rather definitely shown to be that of a plane equilateral triangle with the symmetry D_{3h}. This follows from its zero dipole moment[3] and the results of electron diffraction experiments.[4] The results of the present investigation are in agreement with the assumption that the other boron trihalides also have the symmetry D_{3h}.

The BX_3 molecule then has the four symmetry modes of vibration indicated in Fig. 1. $\nu_1\{1\}$, $\nu_3\{2\}$, and $\nu_4\{2\}$ are allowed in the Raman effect with the depolarizations 0, 6/7, and 6/7, respectively.[5] Numbers in braces adjoining ν's are degeneracies. $\nu_2\{1\}$, $\nu_3\{2\}$ and $\nu_4\{2\}$ are active in the infrared. The selection rules for simple combinations and overtones obtained by the methods of group theory[6] are indicated in Table I.

The fact must be borne in mind that the presence of the isotopes of boron B^{11} and B^{10} in the approximate ratio of 4 to 1 will produce a doubling of those frequencies in which the boron atom moves appreciably. Thus in the Raman effect we should expect ν_3 and $2\nu_2$ each to appear as a doublet separated in frequencies by about 5 percent, and with the lower frequency about four times as intense as the higher. Analogous splits in frequencies should appear in the infrared spectrum with a ratio of extinction coefficients for the two components of 4 to 1. A normal coordi-

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[1] Bhagavantam, Ind. J. Phys. **5**, 73 (1930); Venkateswaran, ibid. **6**, 284 (1931).

[2] A. B. D. Cassie, Proc. Roy. Soc. **A148**, 87 (1935).

[3] E. Bergmann and L. Engel, Physik. Zeits. **32**, 425 (1931); H. Ulich and W. Nespital, Zeits. f. Elektrochem. **37**, 559 (1931); W. Nespital, Zeits. f. physik. Chemie **B16**, 153 (1932).

[4] L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936); private communication.

[5] E. B. Wilson, Jr., J. Chem. Phys. **2**, 432 (1934).

[6] E. Wigner, Gött. Nachr., 133 (1930); G. Placzek, *The Structure of Molecules* (Blackie and Son, London, 1932); L. Tisza, Zeits. f. Physik **82**, 48 (1933); E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934).

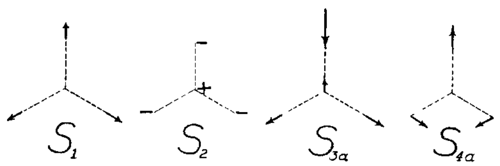

FIG. 1. Symmetry modes of the plane symmetrical BX_3 molecule.

nate treatment should enable one to predict the isotopic doubling of frequencies with greater accuracy.

EXPERIMENTAL

Boron trifluoride was prepared by treating ammonium fluoborate with concentrated sulfuric acid and heating. The reaction chamber was of glass, so silicon tetrafluoride was expected as an impurity. To prepare ammonium fluoborate, boric acid was treated with hydrofluoric acid in a copper beaker; the solution was neutralized with NH_4OH and concentrated by heating. Upon cooling the solution, NH_4BF_4 crystallized out. The BF_3 so prepared was fractionated repeatedly; the final product had a melting point of $-127\pm1°$, in good agreement with the value given in the literature. The Raman spectrum of the somewhat cloudy liquid under its own vapor pressure of 6 atmospheres at the temperature of a solid carbon dioxide alcohol bath was taken using a technique similar to that previously employed for phosphorus trifluoride.[7] The Raman spectrum of the gas at a pressure of six atmospheres was taken using the 2537A line of mercury as a source of radiation. The spectrum from the gas was much more satisfactory than that from the liquid.

Kahlbaum's C.P. boron trichloride (b_{760} 12.5°) was distilled into a Raman tube and sealed in without further purification. The Raman spectrum was obtained at room temperature from the liquid under its own vapor pressure. The polarizations of the two most intense lines were roughly determined. For this purpose[8] the mercury lamp was placed below the horizontal Raman tube with a series of parallel vanes of black cardboard between lamp and tube to insure that the light entering the tube was parallel. The scattered light from the Raman tube then passed successively through a half-wave plate for 4400A, a large Nicol prism with vertical axis, and a lens which focused the light on the 0.4 mm slit of the spectrograph. With the axis of the half-wave plate at an angle of 45° to that of the Nicol, only horizontally polarized light from the Raman tube passed through to the slit. When the axis of half-wave plate and Nicol were parallel, only the perpendicular component reached the slit. The advantage of this arrangement is that all light entering the spectrograph is vertically polarized so that there is no effect of selective transmission or reflection of the light from the slit or prism faces, in contrast to previously used arrangements. Two one-hour exposures were made on the same photographic plate with the two settings of the half-wave plate. Relative intensities of the lines in the two spectra were estimated visually and compared with the relative intensities of the Rayleigh lines which are known to be polarized.

Boron tribromide (b_{740} 90.1°) was prepared by passing bromine vapor over a mixture of boric oxide and carbon at 250°. It was carefully fractionated, the fraction used having a boiling point of $91.0\pm0.2°$. Difficulty was had in sealing the material in the Raman tube without the liberation of small amounts of bromine. The bromine was therefore removed by sealing a small amount of mercury in the Raman tube with the boron tribromide. The mercurous bromide, which was formed on shaking, settled out nicely and Raman spectra of the clear colorless liquid remaining were obtained.

TABLE I. *An addition table showing the selection rules for simple combinations and overtones of modes of vibration of BX_3 molecules.*

	$\nu_1\{1\}R$	$\nu_2\{1\}I$	$\nu_3\{2\}RI$	$\nu_4\{2\}RI$
$\nu_1\{1\}R$	R	I	RI	RI
$\nu_2\{1\}I$		R*	R	R
$\nu_3\{2\}RI$			RI	RI
$\nu_4\{2\}RI$				RI

R indicates a Raman active combination; *I* indicates an infrared active combination.
* $3\nu_2$ is infrared active.

RESULTS AND ASSIGNMENT OF FREQUENCIES

The observed Raman frequencies and assignments are presented in Table II. We shall discuss

[7] D. M. Yost and T. F. Anderson, J. Chem. Phys. 2, 624 (1934).
[8] The arrangement here described, which has been in use in this laboratory for some time, was developed by Dr. Fred B. Stitt of this laboratory. He will publish a more detailed account shortly.

first the more complete results for BCl_3 and proceed then to a discussion of BBr_3 and BF_3.

Boron trichloride

The results for boron trichloride agree with those obtained by Venkateswaran[1] with the exception that the broad band he observed at 947 cm^{-1} is resolved into a triplet. This group, consisting of a sharp line and two broad lines, is reproduced in Fig. 2. The depolarization of the 471 cm^{-1} line was found to be less than 0.25; it was therefore assigned to the mode ν_1. The depolarization of the line at 253 cm^{-1} was close to unity and it was therefore taken to be ν_4. The frequency ν_3 was taken to be the expected isotopic doublet 946, 989 cm^{-1}, the broadness of this pair distinguishing it from the sharp line at 902 cm^{-1}. The latter frequency was then assumed to be $2\nu_2$ whose weaker isotopic component is obscured by the 946 cm^{-1} frequency.

When we make the assignment of infrared absorption frequencies[2] indicated in Table III, we arrive at the values for the vibrational frequencies for $BCl_3(g)$ indicated in Table II. These frequencies differ only slightly from the Raman frequencies for $BCl_3(l)$. The agreement between observed and calculated frequencies is quite satisfactory with the exception of the assignment of the frequency 845 cm^{-1}. Its nearness to the frequency 834 cm^{-1} observed in the Raman spectrum of phosgene[9] and the fact that phosgene is often a by-product in the preparation of BCl_3 and difficult to separate from it, suggest that the presence of this band may be due to a trace of phosgene in the BCl_3 used. The infrared spectrum of phosgene has not been reported. The weaker isotopic components of $\nu_3+\nu_4$ and of $\nu_1+\nu_3$ are evidently too weak to be observed, while that of $3\nu_2$ is obscured by $\nu_1+\nu_3$ from $B^{11}Cl_3$. In other cases the estimated relative intensities of the bands are in accord with the relative abundancies of the boron isotopes. Unfortunately Cassie has not published data from which extinction coefficients could be calculated. The assignment of frequencies is confirmed by the results of the normal coordinate treatment which follows this section.

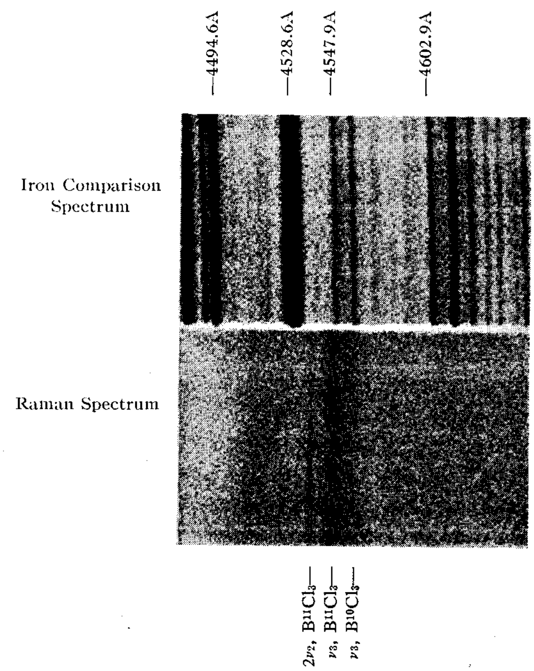

FIG. 2. The effect of the boron isotopes in the Raman spectrum of BCl_3.

TABLE II. *The Raman spectra of boron trifluoride, boron trichloride, and boron tribromide.*

SUBSTANCE	$\nu_1\{1\}$ (cm^{-1})	$2\nu_2\{1\}$ (cm^{-1})	$\nu_3\{2\}$ (cm^{-1})	$\nu_4\{2\}$ (cm^{-1})
$B^{11}F_3(g)$	886(7), 783(3)	1394($\frac{1}{2}$?)*	1038(1)	440(4b) ±25*
$B^{10}F_3(g)$	886(7), 783(3)	(1452)	1105($\frac{1}{2}$?)*	440(4b) ±25*
$B^{11}F_3(l)$	883(1), —	—	—	—
$B^{11}Cl_3(g)$†	471	924	958	243
$B^{10}Cl_3(g)$†	471	(966)	996	243
$B^{11}Cl_3(l)$	471(10)	902(3)	946(3b)	253(8)
$B^{10}Cl_3(l)$	471(10)	(943)	989(1b)	253(8)
$B^{11}Br_3(l)$	279(10)	743($\frac{1}{2}$)	806(3/4b)	151(8)
$B^{10}Br_3(l)$	279(10)	(780)	846($\frac{1}{2}b$)	151(8)

Numbers in parentheses adjoining frequency values indicate relative intensities. b = broad; all other lines are sharp. Numbers in braces adjoining ν's are multiplicities. Frequencies in parentheses are estimated.

* The assignment of these frequencies is provisional for $BF_3(g)$.

† Frequencies obtained from infrared data for $BCl_3(g)$.

[9] Kohlrausch, *Der Smekal-Raman-Effekt* (Julius Springer, Berlin, 1931).

Boron tribromide

The Raman spectrum of boron tribromide is very similar in appearance to that of boron

TABLE III. *The infrared spectrum of boron trichloride.*

$\nu_{obs.}$ (cm^{-1})	$\nu_{calc.}$ (cm^{-1})	Combination
714(4)	714	$\nu_1+\nu_4$
845(3)	834(R)	$COCl_2$ (?)
958(100)	958	ν_3, $B^{11}Cl_3$
996(50)	996	ν_3, $B^{10}Cl_3$
1206(2)	1201	ν_3, $B^{11}Cl_3+\nu_4$
1387(6)	1386	$3\nu_2$, $B^{11}Cl_3$
1429(6)	1429; 1452	$\nu_1+\nu_3$, $B^{11}Cl_3$; $3\nu_2$, $B^{10}Cl_3$
1912(2.5)	1916	$2\nu_3$, $B^{11}Cl_3$
1995(2)	1992	$2\nu_3$, $B^{10}Cl_3$

R = observed in Raman spectrum of $COCl_2(l)$.

TABLE IV. *Calculated force constants K, H, G, and K′, calculated frequencies for trihalides containing B^{10}, and calculated internuclear distances B–X, for boron trihalides.*

SUBSTANCE	$K\times10^{-5}$ (dynes/cm)	$H\times10^{-5}$ (dynes/cm)	$G\times10^{-5}$ (dynes/cm)	$K'\times10^{-5}$ (dynes/cm)	$\nu_3 B^{10}X_3$ calc (cm^{-1})	$\nu_3 B^{10}X_3$ obs. (cm^{-1})	$\nu_4 B^{10}X_3$ calc. (cm^{-1})	$\nu_4 B^{10}X_3$ obs. (cm^{-1})	B–X calc. (A)	B–X obs. (A)
$BF_3(g)$	4.24	0.60	0.88	1.73	1080	1105(?)	416	416*	1.49	1.42†
$BCl_3(g)$	3.30	0.276	0.434	0.653	1000	996	243	243	1.72	1.73
$BBr_3(l)$	2.50	0.252	0.270	0.61	843	846	151	151	1.85	1.87

* This value was assumed for ν_1, $B^{11}F_3$ in order to obtain real values for the constants.
† The sum of Pauling's double bond radii plus 0.04A was taken as an estimate for the B–F distance. See L. Pauling, L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **57**, 2705 (1935).

trichloride with $2\nu_2$ and the isotopic shift of ν_3 both appearing. By analogy with the assignment of the BCl_3 frequencies the assignment of frequencies indicated in Table II was made; confirmation is again obtained from the normal coordinate treatment.

Boron trifluoride

The Raman spectrum obtained from boron trifluoride is much more difficult to interpret. In addition to the frequencies listed in Table II, a line, doubtless due to the presence of SiF_4 ($\nu_1=800(10)$ cm^{-1}),[10] was observed at 801(4) cm^{-1}. The line assigned to ν_4 whose center is at 440 cm^{-1}, is 50 cm^{-1} in width. Its integrated intensity is therefore quite great. We then attribute the strong doublet, which appears as ν_1 in our assignment, to vibrational resonance between ν_1 and $2\nu_4$. Aside from the presence of impurities this appears to be the only reasonable possibility of accounting for the existence of both lines. If we introduce the perturbation term

$$H'=\gamma Q_1(Q_{4a}^2+Q_{4b}^2)$$

(where the Q's represent the normal coordinates and γ is a constant) in the potential energy expression one obtains the following energy levels from the solution of the secular equation:[11]

$$\lambda_1\{2\}=2\nu_4,$$
$$\lambda_2\{1\}=\tfrac{1}{2}[2\nu_4+\nu_1+\{(2\nu_4-\nu_1)^2+8P^2\}^{\frac{1}{2}}],$$
$$\lambda_3\{1\}=\tfrac{1}{2}[2\nu_4+\nu_1-\{(2\nu_4-\nu_1)^2+8P^2\}^{\frac{1}{2}}].$$

We should expect λ_2 and λ_3 to appear, while the simple overtone λ_1 should be very weak in the Raman effect. P, the perturbation energy defined in the usual manner, has the value 35 cm^{-1} when it is assumed that $\nu_1=2\nu_4=835$ cm^{-1}. This value is of the usual order of magnitude for P. The assignment of other observed frequencies is confirmed by the rather satisfying results of the following normal coordinate treatment. An investigation of the infrared absorption spectrum of BF_3 would doubtless yield a unique assignment.

NORMAL COORDINATES; COMPUTATION OF ISOTOPIC SHIFTS IN FREQUENCIES

Normal coordinate treatments of the plane symmetrical AB_3 type molecule have been made by a number of authors.[12] We shall use the valence force potential function V with force constants chosen so that

$$\begin{aligned}2V=K(\Delta R_1^2+\Delta R_2^2+\Delta R_3^2)\\+HR_0^2(\Delta\alpha_{12}^2+\Delta\alpha_{23}^2+\Delta\alpha_{13}^2)\\+GR_0^2(\Delta\beta_1^2+\Delta\beta_2^2+\Delta\beta_3^2)\\+2K'(\Delta R_1\Delta R_2+\Delta R_2\Delta R_3+\Delta R_1\Delta R_3).\end{aligned}$$

R_1 is here the distance $A-B_i$ and R_0 is this distance when the atoms are at equilibrium positions. α_{ij} is the angle B_i-A-B_j while β_i is the angle made by the line $A-B_i$ with the B_3 plane. The frequencies are then given by the equations:

$$m\lambda_1-K-2K'=0,$$
$$mM\lambda_2-(3m+M)G=0,$$
$$\begin{aligned}m^2\lambda_{3,4}^2-\{\tfrac{1}{2}(K-K')(3m/M+2)\\+H(9m/2M+3)\}m\lambda_{3,4}\\+H(K-K')(9m/M+3)=0.\end{aligned}$$

Using the vibrational data for the boron trihalides containing the isotope B^{11} we have determined the various force constants with the

[10] D. M. Yost, E. N. Lassettre, and S. T. Gross, J. Chem. Phys. **4**, 325 (1936).
[11] T. F. Anderson, J. Chem. Phys. **4**, 161 (1936).
[12] D. M. Dennison, Phil. Mag. **1**, 195 (1926); F. Lechner, Wien. Bericht **141**, 633 (1932); J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 630 (1934); J. Rosenthal, Phys. Rev. **47**, 235 (1935). We have applied in part the results of Howard and Wilson in our treatment.

results indicated in Table IV. It is interesting to note that the constant G, usually assumed equal to H in the treatment of pyramidal type molecules, is nearly equal to H for heavy halogen atoms, but is considerably greater than H for light halogen atoms bound to the central boron.

Using these force constants we have calculated the frequencies ν_3 and ν_4 to be expected for the compounds containing the B^{10} isotope. The results agree well with the observed values as indicated in the table. The fact that the frequency ν_4 has little isotopic shift indicates that the symmetry modes are very nearly the normal modes in these cases.

Finally in Table IV, columns 10 and 11 are presented values of the internuclear distances calculated directly from the values of K by Badger's rule.[13] The agreement with the internuclear distances determined by electron diffraction experiments[4] is much better than would have been expected, judging from the experience of previous investigators.

[13] R. M. Badger, J. Chem. Phys. 2, 128 (1934); 3, 710 (1935).

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The Entropy of Carbon Tetrachloride

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A new calculation of the entropy of carbon tetrachloride has been made from Raman spectra and electron diffraction data. The effect of the isotopes of chlorine has been investigated. A new value of the calorimetric entropy has been computed from recent (and in part unpublished) thermal data. The agreement of the entropies is sufficiently good as to leave little reason to doubt the validity of the spectroscopic calculations

SOME time ago Yost and Blair[1] noted a difference of about three entropy units between the entropy of carbon tetrachloride calculated from the existing thermal data[2] and a value of the entropy which they calculated from spectroscopic data by statistical methods. Assuming that the thermal data were substantially correct, they suggested that the discrepancy arose in the statistical calculation from uncertainty about the vibrational states of the molecule. The purpose of their note was to point out the dubious value, in their opinion, of spectroscopic entropy calculations made on the basis of the customary assumption that molecular vibrations are quasi-harmonic. In view of the good spectroscopic data available and the straightforward interpretation of the vibrational structure of carbon tetrachloride, it seemed to us unlikely that uncertainties of the sort suggested by Yost and Blair could account for the discrepancy between the thermal and spectroscopic entropies. Rather it appeared that the difficulty probably lay in the experimental thermal data. We have had put at our disposal some new unpublished heat capacity data for carbon tetrachloride. Furthermore we have made a new calculation of the statistical entropy, thoroughly investigating several possible sources of the disagreement. The theoretical and calorimetric data have been found to agree well within the limits of the probable experimental error in the latter.

STATISTICAL ENTROPY

It appeared worth while to refine the statistical computations by taking into account the isotopes Cl^{35} and Cl^{37}. The presence of these isotopes creates five different isotopic configurations for carbon tetrachloride, and the final value of the entropy has been obtained from the entropies of the configurations. It is to be remarked that the symmetry numbers of the various configurations are not uniformly twelve. At first sight, this variance in symmetry number might be thought

[1] Yost and Blair, J. Am. Chem. Soc. 55, 2610 (1933).
[2] Latimer, J. Am. Chem. Soc. 44, 90 (1922).